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**Revising the
stoichiometry of
mixed layer export**

A. N. Antia

Particle-associated dissolved elemental fluxes: revising the stoichiometry of mixed layer export

A. N. Antia

Leibniz-Institut für Meereswissenschaften, Research Division Marine Biogeochemistry,
Düsternbrooker Weg 20, 24105 Kiel, Germany

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Correspondence to: A. N. Antia (aantia@ifm-geomar.de)

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Abstract

Sinking particles carry substantial loads of dissolved elements in their interstitial spaces that contribute to the vertical transport of elements out of the euphotic zone. Elemental fluxes as traditionally measured by sediment traps underestimate total export when this particle-associated dissolved flux is not considered. The errors introduced are variable and alter both the absolute levels of flux as well as the stoichiometry of export. Using samples from sediment traps in the North Atlantic and measuring excess dissolved carbon, nitrogen, phosphorus, silica and calcium in the supernatant of the collection cups, it is possible to quantitatively assess the total flux in the sample. At the base of the winter mixed layer, up to $90\pm 6\%$ of phosphorus fluxes are found as excess phosphate whereas for carbon and nitrogen dissolved concentrations account for between 30% and 47% of total fluxes respectively. Particle-associated dissolved silica fluxes are a mean of 61% of total flux. Little ($<10\%$) of calcium fluxes are in dissolved form. The proportion of dissolved to total flux decreases with trap deployment depth. Calculations of the C:N:P ratios for particles only are well above the Redfield Ratio of 106:16:1 (Redfield et al., 1964), although the mid-water dissolved N:P and N:Si values as well as the C:N:P ratios of remineralisation along isopycnals conform to the Redfield Ratio at this site. Accounting for dissolved fluxes of all these elements brings the estimates in agreement with the Redfield Ratio and with other geochemical estimates of the stoichiometry of winter mixed layer export. A factor of 3 to 4 higher ratios of organic:inorganic carbon export also implies that the net atmospheric CO_2 sequestration by the biological pump is about 50% higher at this site when the particle-associated dissolved elemental fluxes are considered.

1. Introduction

The biogenic production of particles in the surface ocean leads to incorporation of major and minor elements into organic material or on matrices that, after coagulation

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and aggregation sink out of the upper mixed layer and transport these elements to the deep sea and sea floor. The proportion in which these elements leave the surface mixed layer determines their relative residence times at the surface and their deep-water stoichiometry. Since Redfield et al. (1963) pointed out the relative constancy of carbon, nitrogen and phosphorus (C, N and P) in organic matter and inorganic N:P in the deep sea, this concept has been widely used to estimate fluxes of one element based on those of the others (e.g. MacCreedy and Quay, 2001). Indeed, this ratio is so accepted as being the “norm” that deviations in surface waters are interpreted as “over-production” of carbon, or an elevated efficiency of the biological pump (Körtzinger et al., 2001a; Engel et al., 2002). In the mesopelagial, changes in these ratios with depth are taken to reflect the remineralisation time and length scales of different elements (Honjo et al., 1982; Honjo and Manganini, 1993). Among the other bio-active elements, silica (specifically the N:Si ratio in upwelled water) determines the contribution of diatoms to new production, thus influencing species succession in a way that is important for particle export. Additionally, the ratio of inorganic carbon (primarily calcium carbonate) to organic carbon in particles exported from the winter mixed layer determines the efficiency of net atmospheric CO₂ sequestration (Antia et al., 2001). Both silicate and carbonate are thought to play a prominent role in ballasting material to accelerate its sinking speed (Armstrong et al., 2002; Klaas and Archer, 2002), so their contribution to sedimenting particles can potentially alter the efficiency of bulk export.

Sediment traps, more correctly called particle interceptor traps, have been used for several decades to quantify and characterise the flux of elements from the surface to the deep sea. Despite uncertainties in the efficiency with which traps collect the true settling flux, they are still the sole means by which time-series sampling of sinking particles is done in the mid-ocean. Valuable insights into the close coupling of surface processes with mesopelagic and benthic fluxes as well as novel information on the vertical fluxes of major and minor elements has emerged from trap studies, contributing to our understanding of ocean biogeochemical cycles. Almost simultaneous with the enthusiasm in deploying traps in numerous environments came the sobering realisation

that they fell short of collecting the “true” sinking flux (Gardner, 1980; Buesseler, 1991; Gust et al., 1992, 1996). Of the many issues addressed, hydrodynamic biases appear to be a major problem, causing under- or over-collection of particles and sorting of particles based on size or other properties (Gust et al., 1996). A comprehensive summary of this technology and its caveats is given by Gardner (2000).

A further issue that is less often addressed or corrected for when measuring export fluxes using sediment traps is the dissolution of material after particles settle in the trap cups. A number of early studies report dissolution of organic carbon (Gardner et al., 1983; Noji et al., 1999; Honjo et al., 1995), and nitrogen (Hansell and Newton, 1994; Kähler and Bauerfeind, 2001) amino acids (Lee and Cronin, 1982; Lee et al., 1992), fatty acids (Körtzinger et al., 1994), phosphate (Knauer et al., 1984; von Bodungen et al., 1991), dissolved inorganic nitrogen (primarily ammonium, Knauer et al., 1990; von Bodungen et al., 1991), silicate (von Bodungen et al., 1991; Bauerfeind et al., 1997; Antia et al., 1999) and metals (Knauer et al., 1984; Pohl et al., 2004). Despite finding that dissolution can account for a large and variable proportion of the measured particulate flux, to date there has been no systematic analysis of the corrections that may need to be applied to arrive at values of the entire flux in the trap. As important as errors in the absolute levels of flux are changes in the ratios of the elements to each other, as mentioned above.

When compiling existing data from the literature on dissolved compounds in trap supernatant, it became apparent that while some studies had looked at individual compounds no comprehensive data existed in which the major elements were measured for a single set of samples. The aim of this study was to estimate the degree of dissolution of major elements (carbon, nitrogen, phosphorus, silica and calcium) from particles captured by sediment traps at different depths from long-term moorings in the North Atlantic and assess how this process affects the estimation of the stoichiometry of export.

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2. Materials and Methods

Conical, 0.5 m² aperture Kiel-type sediment traps were deployed on 3 moorings at the European continental margin at depths between 600 m and 4000 m. Details of mooring deployment and sample processing are given in Antia et al. (1999). Sedimentation rates of particulate organic carbon and nitrogen (POC and PON) and particulate biogenic silica (PSi) presented here are available from the OMEX database (<http://www.bodc.ac.uk/projects/omex.html>). Particulate organic phosphorus (POP) was measured after filtration, oxidation and colorimetric determinations after Grasshoff et al. (1999).

Seawater from ca. 1000 m depth at the mooring sites, with 0.14% mercuric chloride added as a poison was used to fill the trap jars prior to deployment. Dissolved carbon, nitrogen, phosphorus and silicate was measured in this water and these values were used as background concentrations. After recovery and transport to the laboratory, samples were placed upright and particles allowed to settle to the bottom of the cups before further analyses. Supernatant water from above the particle pellet was carefully pipetted out, filtered through sterile 0.45 µm polycarbonate filters and stored at 4°C in the dark. Samples were processed in the order in which they were exposed in the traps so that, including time of deployment and time between recovery and processing, all samples had been in the poisoned jars for at least 5 months before analysis.

The following was analysed in supernatant: nitrate, nitrite, ammonium, silicate and phosphate, dissolved organic carbon (DOC) and nitrogen (DON) and dissolved calcium. NO₂, NO₃, NH₄, PO₄, SiO₄ were analysed using the manual methods described in Grasshoff et al. (1999). Samples were diluted 1:10 before nitrate analyses to keep the level of mercuric chloride below 0.02%, so as not to compromise the efficiency of the cadmium reductor. DOC and DON were analysed using the high temperature catalytic oxidation (HTCO) method and dissolved calcium using ICP analyses. Dissolved organic phosphorus was measured in 119 samples as the increase in phosphate concentration after treatment with a strong oxidising agent (Oxisolv, Merck).

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The excess dissolved concentration of each element in supernatant was calculated as the difference between the measured value and the background value in water used to fill the sample cups. Total fluxes were calculated from the sum of dissolved and particulate flux of each element. In several cases and in particular for phosphorus, mean fluxes showed large variations due to extreme outliers in the data. These were defined as values lying outside of three standard deviations from the mean and discarded from calculations. Generally 0, 1 or 2 outliers per set of 21–40 values were identified and eliminated.

Adding to the data analysed from the OMEX traps literature values were taken from trap deployments in the North Atlantic and Southern Ocean. Data from the Greenland and Norwegian Seas were provided by the Special Research Project (313) of the University of Kiel and are available under <http://www.ifm.uni-kiel.de/jgofs/dm/>. Data from traps in the Southern Ocean are from the SAZ Project of the Antarctic CRC, Australia (Bray et al., 2000). The sources of other data compiled for comparison are given in the legend of Table 1.

3. Results

3.1. Excess phosphorus in supernatant

For all elements examined, substantial excess dissolved concentrations in supernatant were found. This was most pronounced for phosphorus, with up to 90 (± 6.4)% of the total phosphorus in trap jars found as excess phosphate (DIP_{ex}) in supernatant at 600 m at the OMEX 3 site (Fig. 1a, Table 1). Excess dissolved organic phosphorus could not be detected, with a mean measured concentration of $1.04 (\pm 2.7) \mu\text{mol dm}^{-3}$. With increasing trap depth the proportion of DIP_{ex} to total phosphorus found in the cups decreased substantially, accounting for 61 (± 20.4)%, 34 (± 23)% and 15 (± 3.4)% of total phosphorus at 1440 m, 3220 m and 4000 m respectively. Site-specific differences in dissolved phosphorus fluxes between these traps and literature values were

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small, with a similar proportion of total phosphorus as DIP_{ex} at two sites in the Norwegian Sea and East Greenland Sea (ca. 80% at 500 m, decreasing to 68 and 40% at 3000 m and 2200 m respectively, Table 1, see also von Bodungen et al., 1991). Lower dissolved fluxes were found in the temperate North Atlantic at 34° N and 48° N (21° W), decreasing from 30–50% at 1000 m to 17% at 3700 m and 10% at 4500 m. Weak linear correlations between particulate organic phosphorus and DIP_{ex} were found at all sites.

Since samples were processed a minimum of 5 months after sample retrieval a time-course of increase in dissolved elemental concentrations in supernatant could not be investigated. After the initial analyses in 1994, splits and supernatant were stored at 4°C in the dark and reanalysed in 2004 for selected variables. During this long-term storage particulate organic phosphorus showed no decrease, indicating that further degradation or leaching did not occur. For particulate organic phosphorus measured in 1994 (POP_{1994}) and the measurements repeated in 2004 (POP_{2004}) the following relationship was found:

$$POP_{1994} = 0.09(\pm 0.07) + 1.03(\pm 0.28) POP_{2004}; n = 136, r^2 = 0.89.$$

3.2. Excess silica in supernatant

High excess dissolved silica (DSi_{ex}) concentrations were found in all traps studied (Fig. 2). Maximum DSi_{ex} values in supernatant of ca. 1000–1200 $\mu\text{mol/l}$ (at which concentration silicate saturates in seawater at ca. 2°C and pH 8, Rickert et al., 2002) were seen, with the initial slope of PSi to DSi_{ex} decreasing with increasing water depth. Maximal losses of DSi to the dissolved phase at the 500 m horizon amounted to between 61 (+7.4)% at the OMEX 3 site and 35 (+21.1)% in the Norwegian Sea. Below 3500 m a relatively constant 6.1–6.7% of the total siliceous flux was found as DSi_{ex} (OMEX 4 at 4000 m; 34° N, 21° W at 4500 m; 47° N, 21° W at 3700 m). Remarkably low dissolution of SiO_4 into supernatant (<5 to 10%) was seen in traps from the Southern Ocean at 51° S and 53° S, up to an order of magnitude lower than the other sites at similar depth.

3.3. Excess nitrogen in supernatant

For nitrogen too substantial excess concentrations in supernatant were seen. Excess dissolved inorganic nitrogen ($\text{DIN}_{\text{ex}} = \text{excess NO}_3 + \text{NH}_4$) was low (ranging from 1.5 to 5.4% total nitrogen, Fig. 3a–d and Table 1) and consisted almost exclusively of ammonium. Excess dissolved organic nitrogen (DON_{ex}) accounted by far for the larger part of dissolved nitrogen species and amounted to 45 (+13)% and 16.7 (+2.9)% of total nitrogen fluxes in the traps at 600 m and 4000 m respectively (Fig. 4a). DON_{ex} was linearly related to PON fluxes and showed a decreasing trend as proportion of total nitrogen flux with trap depth.

3.4. Excess carbon in supernatant

A similar trend was observed for excess dissolved organic carbon (DOC_{ex}) in supernatant, in that it was linearly related to POC flux and decreased with increasing trap depth (Fig. 4b). Altogether, 30 (+6.6)% and 7 (+3.6)% of total carbon was found as DOC_{ex} at 600 m and 4000 m respectively. We did not measure dissolved inorganic carbon (DIC) in supernatant, but the sea water was well buffered ($\text{pH} > 7.6$) leading us to assume no significant DIC increase. Production of DIC through microbial activity would indicate ineffectiveness of the trap poison, which at the levels used (0.14% HgCl_2) stop bacterial activity within hours (Lee et al., 1992). We did however, measure excess dissolved Ca (DCa_{ex}) to check for inorganic carbon losses; on average there was an increase of 3.9–7.9% above background dissolved Ca levels (9.9% at 1440 m).

3.5. Swimmer-related excess dissolved fluxes

For the trap at 600 m, where maximal swimmers were found, there was no correlation between swimmer carbon (a better estimation of swimmer flux than number alone) and DOC or DON values ($r^2 = 0.17$, $n = 37$). At this depth, swimmer biomass was low compared to total organic carbon and nitrogen fluxes, accounting for a mean of 10.9

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(± 7.1)% of total carbon (DOC+POC) in the traps. Even assuming that 20% of the swimmer biomass leached into the surrounding seawater, this effect would be negligible on DOC increase. I therefore neglect swimmer-derived DOC/N and assume all the excess DOC and DON originated from organic particles.

5 3.6. Correction of C:N:P, N:Si and POC:PIC ratios

Table 2 summarises the molar ratios of C:N:P for the traps analysed in this study as well as other values from the literature. Relying on information from particulate analyses only, the C:P and N:P ratios are highly in excess of the Redfield value of 106:1 and 16:1 respectively, even though the scatter in the data is large. Where corrections for the dissolved fluxes are available for all elements, mean ratios at the base of the mixed layer are well in agreement with the Redfield ratios, increasing with depth to 4000 m. Large shifts in the POC:PIC ratio are seen when accounting for excess dissolved fluxes, increasing from 2:1 to a mean of 7:1 at 600 m. For nitrogen and silica, similar rates of dissolution result in large corrections of the absolute flux values but the ratio of N:Si remains unchanged (Table 3).

4. Discussion

The fact that large sinking aggregates, the main vehicles for vertical elemental fluxes (McCave, 1975; Fowler and Knauer, 1986), carry with them dissolved loads in their interstitial spaces has been recognised for some time. Aggregates are greatly enriched in DOM and inorganic products of remineralisation and dissolution such as phosphate and silicate (Shanks and Trent, 1979; Alldredge, 2000; Brzezinski et al., 1997). A substantial amount of the dissolved loads leave the aggregates within the euphotic zone (Kjørboe et al., 2001), since diffusion between the aggregate and seawater are high (Alldredge and Cohen, 1987; Ploug et al., 2002). Fecal pellets, an important aggregate type, also contain large amounts of DOM that rapidly leach out into the surrounding sea

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water (Lampitt et al., 1990; Urban-Rich, 1999). Packed with bacteria and heterotrophic protozoa (Silver and Alldredge, 1981; Simon et al., 2002), these micro-environments are hotspots of microbial activity in the water column (Grossart and Ploug, 2001) and greatly affect the cycling of elements in the water column. Investigating the time-course microbial degradation of fesh diatom aggregates, Grossart and Ploug (2001) find significant carbon and nitrogen contents and high microbial turnover rates after 8 days of incubation, during which time aggregates in the natural environment would be well below the winter mixed layer.

As Alldredge (2000) points out, the dissolved loads in the interstitial spaces of aggregated must contribute substantially to vertical flux. However, practically all measurements of DOM within aggregates have been done within the upper water column; the DOM load in sub-surface and deep aggregates is unknown. The data presented here provide a first, albeit indirect, estimate of dissolved elemental concentrations in large particles in the mid- and lower water column.

Aggregates are thus carriers of significant amounts of dissolved material, here called the “particle-associated dissolved flux”. In sediment traps, these particles settle into trap jars where microbial activity is stopped or greatly reduced depending on the preservative or poison used. At the concentration of mercuric chloride used in this study Lee et al. (1992) report complete and almost immediate cessation of microbial activity. I assume, thus, that the excess dissolved concentrations in supernatant water are not an artefact produced by degradation of material within the cups but result solely from passive leaching of material that arrived in the trap in the interstitial spaces of particles. Diffusive fluxes on the order of ca. 16–50 $\mu\text{m}/\text{day}$ (Kjørboe et al., 2001; Ploug et al., 2002) would ensure equilibration of interstitial concentrations with the supernatant solution during the long storage times used in this study. Even assuming lower diffusion rates due to the presence of a polysaccharide matrix and the fractal nature of aggregates (Alldredge, 2000), for long-term moorings the diffusion rate will not limit the net leaching of dissolved substances out of the particles. During further processing of the samples (picking of swimmers, splitting and filtering), particles are rinsed with

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seawater and partially broken, and particularly during filtering the interstitial spaces are bled. However, presuming equilibrium between the particles and surrounding seawater, adding the excess elemental fluxes to the measured particulate flux accounts for this loss. Filtration of particles prior to analysis, whether from water bottles, trap jars or in situ pumps, causes loss of interstitial fluids and underestimation of their elemental loads. This “particle-associated dissolved load” is not measured in either the particulate or dissolved pool using current protocols, and is potentially lost in estimates of elemental standing stocks and vertical flux. This caveat is common to all analyses of particles in the water column and warrants attention in all biogeochemical studies.

The data here show agreement with those of Alldedge (2000) who measured POC and DOC on aggregates from 2–20 m water depth. At these shallow depths DOC was on average 31% of total carbon in the particles whereas in trap material at 600 m depth (this study) DOC_{ex} was on average 30% total carbon in the cups, suggesting that a significant proportion of labile organic carbon is still being recycled within aggregates reaching the base of the mixed layer, and that losses due to leaching, diffusion and assimilation by organisms on and in the aggregates are lower than the net DOC production rates. Considerably lower DOC_{ex} , accounting for <10% total carbon, is exported below 1400 m. The linear relationship between POC flux and DOC_{ex} implies no significant seasonality in the contribution of dissolved matter to total fluxes, but rather a constant internal aggregate remineralisation by bacteria and protozoa, in proportion to organic matter availability.

For silica and calcium, where dissolution is controlled both by physico-chemical factors as well as biological degradation, dissolution and leaching may continue after microbial activity is stopped. Silica dissolution on organic aggregates is accelerated by destruction of the organic frustule matrix through bacterial protease activity (Bidle and Azam, 2001), and diatomaceous aggregates in the upper water column accumulate silicic acid in their interstitial spaces at upto 100-fold higher concentrations than in the surrounding seawater (Brzezinski et al., 1997). Although seawater is greatly undersaturated with respect to silicic acid, high siliceous fluxes and leaching out of particles

cause saturation of silicate in supernatant water (Fig. 2), presumably stopping further losses due to passive dissolution.

For calcite, losses from the particles are low and relatively constant. Lower dissolution of this inorganic carbon compared to the high DOC_{ex} concentrations alter the Corg:Cinorg ratio (rain ratio) of flux at the base of the winter mixed layer (Table 2), that is responsible for net drawdown of atmospheric CO_2 by the biological pump. Net carbon (sequestration) fluxes at the winter mixed layer at the OMEX site as defined and calculated by Antia et al. (2001) increases by 50% from 1.47 to 2.22 $\text{mgC m}^{-2} \text{yr}^{-1}$ in reponse to the increase in the rain ratio from 2 to 8 at 600 m depth when accounting for the particle-associated dissolved fluxes (Table 2).

Factors such as fixative/poison type, brine, buffer, and presence of swimmers are likely to affect leaching of interstitial fluids. Where data are available (Table 1), in traps with similar treatments (mercuric chloride, no brine addition), similar proportions of excess dissolved phosphorus and silicate were found in supernatant at similar depths. For silicate, traps in the southern Ocean showed lower DSi_{ex} concentrations; however, since both the species composition and biogeochemical regimes as well as trap treatment (addition of brine) differed, it is difficult to separate these effects. For traps at similar sites and depths, (the OMEX traps and data from Honjo and Manganini, 1993) there are factor of 2 differences in the slopes of dissolved to particulate fluxes of phosphorus and silica measured (Figs. 1 and 2), with much higher proportions of dissolved elements in the HgCl_2 -poisoned OMEX traps. These may be due to differences in poison/fixative used since formalin is known to stabilize membranes and chitinous structures, possibly making them less permeable for leaching (e.g. Lee et al., 1992). Rather unfortunately, the use of formaldehyde as a fixative, as recommended by the JGOFS protocols (http://usjgofs.whoi.edu/protocols_rpt_19.html) precludes DOC/DON measurements in supernatant, the effect of which can be substantial in the mesopelagic zone.

For silica in particular, the initial slope of DSi_{ex} against P_{Si} flux varies both with depth and site. At 51° S in the polar front where the large, heavily silicified *Fragillariopsis*

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kerгуelensis dominated diatom export (Bray et al., 2000; T. Trull, pers. comm.) about half the silica dissolution of that found at other sites at the same depths was seen. Such site-specific differences in dissolution of biogenic silica has been reported by Rickert et al. (2002) who found a factor of 10 lower dissolution of silica in the Southern Ocean compared to the Norwegian Sea, related to differences in the reactivity of diatom shells. Species-specific differences in the dissolution of diatom frustules (Kohly, 1998), and strong differences in reactivity of biogenic silica linked to the structural integrity, organic coating and detrital minerals is manifested in higher silica contents of Southern Ocean sediments compared to similar latitudes in the North (Schlüter et al., 2000).

Although in this study swimmer fluxes were low and negligible compared to the passive sinking fluxes, swimmers may strongly falsify results in shallow traps (Steinberg et al., 1998). Addition of brine, that causes zooplankton swimmers to herniate in the traps, (Peterson and Dam, 1990) would magnify the problem. Since swimmers, through herniation, excretion and leaching will introduce large dissolved concentrations that cannot reliably be separated from the particle-associated dissolved load, swimmer avoidance should be a priority.

For elements other than those presented here, the rate and degree of dissolution would need to be individually determined. Knauer et al. (1984) shows rapid dissolution of up to >80% and >70% of sedimenting Manganese and Cadmium respectively and similarly high dissolution, although proceeding at a slower rate, for Zinc. Pohl et al. (2004) find only half those values in their traps. Particle-reactive elements such as iron and thorium are, predictably, not found in supernatant (Pohl et al., 2004).

Given the differing stoichiometry of POM and DOM and the differing time scales of their production and mineralisation (Hopkinson and Vallino, 2005) large aggregates as carriers of both particulate and dissolved material should be treated as a single entity requiring a consolidated analytical approach. This would include collection of interstitial waters during filtration with analyses of excess dissolved elements, as has been done in the upper water column in but relatively few studies.

Correcting for loss of particle-associated dissolved elemental fluxes can have severe

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to negligible effects depending on element and trap depth, both in terms of the absolute values of flux as well as in the stoichiometry of settling material (Table 3). Whereas at the base of the winter mixed layer at around 500 m, phosphorus would need to be corrected upwards by a factor of up to 10, carbon and nitrogen flux corrections are between factors of 1.4 to 2. Slightly higher dissolution of silica would make the total silica fluxes higher by a factor of 2 to 2.5. Total calcium fluxes are practically unaffected by dissolution. These estimates are similar to the errors due to hydrodynamic biases of moored traps, estimated by water column radioisotope budgets (Scholten et al., 2001; Yu et al., 2001) below the mixed layer. Both these effects (particle-associated dissolved fluxes and hydrodynamic biases) decrease with increasing water depth and when accounted for, will increase the estimates of mid-water remineralisation rates that have arisen from sediment trap data (e.g. Pace et al., 1987; Martin et al., 1987; Antia et al., 2001). These “corrections” may narrow the gap between measured particle fluxes and those based on subsurface oxygen utilization rates (Jenkins, 1982). They would also substantially decrease the estimated “lateral” or “advective” fluxes that are assumed where an increase in flux with depth is measured. (e.g. Antia et al., 1999; Neuer, 1997) and narrow the observed discrepancy between vertical POC fluxes and sediment community carbon demand (Lampitt et al., 1995; Smith et al., 2001)

The ratio of major elements (organic- and inorganic carbon, nitrogen, phosphorus and silica) leaving the upper mixed layer is crucial in estimating the net sequestration potential of the biological pump and the global distribution of deep-water nutrient ratios. Biogeochemical models routinely use nitrate fluxes to estimate carbon export (e.g. MacCreedy and Quay, 2001) relying on the mean global validity of the Redfield stoichiometry of C:N uptake in the formation of primary organic matter. Although there is evidence that, at least seasonally, particle formation with a C:N ratio significantly higher than the Redfield Ratio takes place (Körtzinger et al., 2001; Engel et al., 2004) this analysis indicates that export at the base of the mixed layer does not reflect this in the annual mean, at least in the North Atlantic.

A large amount of data on the elemental ratios of sinking particles arises from sedi-

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ment traps (summarized in Table 2) and uniformly shows C:N ratios above the Redfield Ratio at the base of the mixed layer. In a compilation of trap and in situ pump data Schneider et al. (2003) report C:N ratios above 8.5 below 500 m depth, increasing by 0.2 per 1000 m. The OMEX data reported here are in agreement with this trend for the particulate fraction only (Table 1). Correcting for dissolved C, N and P in the traps however gives total elemental ratios of almost exactly 106:16:1. C:N ratios not significantly different from the Redfield Ratio ($6.1 \pm 1.2:1$) at 600 m depth at this site are also in agreement with those calculated by Körtzinger et al. (2001) along isopycnals at similar depths in the North Atlantic (6.5 ± 0.2). Körtzinger et al. (2001) in turn revised the previously lower estimate (C:N of $5.1 \pm 0.2:1$) of Takahashi et al. (1987) by subtracting the contribution of anthropogenic CO_2 to total DIC. Total N:P ratios of ca. 16:1 and N:Si ratios of 2.4:1 in sedimenting particles at the base of winter mixed layer agree with long-term means of dissolved nutrients in the mesopelagic zone at this site (data from the Levitus Web site <http://ingrid.ldeo.columbia.edu/SOURCES/.LEVITUS/>), that provide a constraint to the ratios of export from the upper mixed layer.

Phosphorus fluxes are seldom reported in sediment trap studies, and indeed the extremely high C:P and N:P ratios found in the particulate fraction only (Table 1) are difficult to interpret. Even accounting for the more rapid remineralisation and loss of phosphorus from sinking particles compared to carbon and nitrogen, mid-water phosphate values present a constraint to loss rates that are far below those implied by N:P ratios of over 50:1 at the base of the mixed layer (Table 2). At the OMEX sites, revising the elemental export values to account for particle-associated dissolved fluxes brings the values in agreement with mid-water N:P and N:Si ratios of 16:1 and 3:1 respectively (calculated from the Levitus data set). The ability to measure the N:P and C:P ratios of export is useful especially in regions where nitrogen is in chronic under-supply to the euphotic zone, and in coastal regions where phosphorus can limit growth. The commonly assumed excess carbon over nitrogen and nitrogen over phosphorus in winter mixed layer export reported from sediment traps may largely be an artifact of the measurements though more data are needed to confirm this conclusion from other

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sites.

Biogeochemical studies investigating the efficiency of the biological pump in atmospheric CO₂ sequestration concentrate on the export of carbon to the limiting nutrient in excess of the Redfieldian value since this would supposedly enhance the oceans' role in the current climate debate. Should much of the “excess” fixed carbon be labile and respired near the surface, as is thought for the carbon-rich polysaccharide exudates of phytoplankton (Passow, 2002) this will have little effect on net carbon export. Possible sites of over-Redfield carbon export to below the mixed layer are thus most likely in the upwelling and high-productivity regions of the Tropical Ocean, where annual mixing is shallow and highest net sequestration fluxes are found (Antia et al., 2001). If sediment traps can be used to more reliably estimate the stoichiometry of export, a range of other analyses in the sedimenting particles they collect could give valuable insight into the biological control of export and regional deviations from the global mean. This warrants attention in further studies.

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Table 1. The contribution of dissolved carbon, nitrogen, phosphorus, calcium and silica to total (particulate + excess dissolved) fluxes in sediment traps below the winter mixed layer.

Site	Depth	DOC (%TC)	DON(%TN)	DIN (%TN)	DIP(%TP)	dCa(%totCa)	dSi (%total Si)	Brine	Poison
	(m)	Mean±SD	Mean±SD	Mean±SD	Mean±SD	Mean±SD	Mean±SD		
European Continental Margin ¹	600	29.9±6.6	44.5±10.5	2.8±2.5	85.8±18.6	7.7±4.9	42.9±20.0	no	HgCl ₂
"	1100	28.3±9.0	44.4±10.8	3.9±1.1	70.6±18.3	7.5±5.3	33.2±11.6	no	HgCl ₂
"	600	28.2±8.2	45.4±45.4	1.7±1.0	90.4±6.4	7.5±5.0	60.9±7.4	no	HgCl ₂
"	1440	17.2±9.2	29.4±9.8	5.4±1.6	61.6±20.4	9.9±3.4	35.9±16.5	no	HgCl ₂
"	3200	9.3±6.8	12.0±7.3	4.5±2.6	34.4±22.7	8.0±5.4	21.9±10.4	no	HgCl ₂
"	4000	7.1±3.6	16.7±2.9	1.5±0.4	15.5±3.4	3.9±2.1	6.7±2.4	no	HgCl ₂
46.45° S; 142.4° E ²	1000						24.5±10.1	yes	HgCl ₂
"	2000						18.6±7.6	yes	HgCl ₂
"	3800						23.8±9.4	yes	HgCl ₂
51.0° S; 141.44° E ²	3300						9.9±5.5	yes	HgCl ₂
53.44° S; 141.45° E ²	800						4.9±2.3	yes	HgCl ₂
"	1500						8.3±3.7	yes	HgCl ₂
34° N; 21° W ³	1071/1248				33.2±21.5		19.8±13.5	no	Formalin
"	2067/1894				26.1±18.9		9.8±5.4	no	Formalin
"	4564/4391				10.1±6.1		6.7±3.0	no	Formalin
48° N; 21° W ³	1081/1202				51.1±15.1		10.2±4.4	no	Formalin
"	2018/2200				31.8±12.5		7.7±4.9	no	Formalin
"	3718/3749				17.3±10.8		6.1±2.9	no	Formalin
Norwegian Basin ⁴	500				79.6±13.6		34.9±21.1	no	HgCl ₂
"	800				72.5±19.7		37.9±21.6	no	HgCl ₂
"	3000				68.6±18.4		12.3±6.3	no	HgCl ₂
East Greenland Sea ⁴	500				78.4±16.5		35.0±17.7	no	HgCl ₂
"	1000				64.7±36.1		35.7±18.7	no	HgCl ₂
"	2200				39.7±23.0		22.9±15.0	no	HgCl ₂
"	500							no	HgCl ₂
"	1000							no	HgCl ₂
"	2200							no	HgCl ₂
Equatorial Pacific ⁵	700	56.0						yes	NaN ₃
"	800						18.7	yes	NaN ₃
"	800						21.7	yes	NaN ₃
"	800						21.4	yes	NaN ₃
Equatorial Pacific ⁶	1095				74±3				
"	1895				70±3				
"	3495				50±13				
"	700				70±8				
"	1600				49±16				
"	3000				26±10				
Greenland Basin ⁷	180/275	33						no	HgCl ₂
"	775/900	50						no	HgCl ₂
"	1735/2100	63						no	HgCl ₂
Greenland Sea ⁸	500			7.8–38	94–98		45–55	no	HgCl ₂

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Table 2. POC:PIC and atomic N:Si ratios from the particulate fraction only and total (particulate + particle-associated dissolved) material in sediment traps.

Site	Depth (m)	Ratio in partiCles only		Ratio in total material	
		POC:PIC	N:Si	C _{org} :C _{inorg}	N:Si
European Continental Margin	600	2,0±1,2	2,2±1,1	6,1±3,3	2,4±1,3
"	1100	2,1±1,9	1,3±0,9	6,4±3,5	1,3±0,8
"	580	2,1±0,6	3,4±1,9	8,0±1,7	2,5±1,3
"	1440	2,8±2,5	0,9±0,6	4,3±1,7	1,0±0,5
"	3220	1,3±0,8	0,4±0,2	2,6±1,1	0,4±0,2
"	4000	0,8	0,4	1,1	0,4

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Table 3. Atomic C:N:P ratios from the particulate fraction only and total (particulate + particle-associated dissolved) material in sediment traps and from chemical analyses along isopycnals.

Site	Depth (m)	Ratio in Particles Only				Ratio of Total Flux			
		C:	N:	P	C:N	C:	N:	P	C:N
European Continental Margin ¹	600	724±353	85±30	1	8.3±2.0	104±70	17±7.9	1	5.6±1.6
"	1100	464±291	56±33	1	9.1±2.0	187±110	25±8.4	1	6.5±1.6
"	580	915±426	94±44	1	9.2±2.1	107±69	15±8.0	1	6.1±1.2
"	1440	524±338	52±32	1	9.6±2.9	206±130	30±17.6	1	6.9±1.9
"	3220	317±181	33±16	1	9.7±2.4	236±112	29±12.5	1	7.8±2.1
"	4000	282	26	1	11.3	196	28	1	8.1
Norwegian Basin ²	400	730	49	1	16.3				
"	800	321	25	1	13.1				
"	2950	345	17	1	22.6				
East Greenland Current ³	500	647	59	1	9.6				
"	500	1053	84	1	9.4				
"	500	622	71	1	8.2				
"	1000	331	33	1	8.5				
"	2200	226	30	1	8.9				
"	2310	171	19	1	10.3				
Gulf of Riga ⁴	30	426	49	1	9.3				
Gotland Sea ⁵	140	82	9	1	9.3				
N. Baltic Sea ⁶	40	9 to 13	5 to 22	1					
SargassoSea ⁷	150	457	46	1	8.6				
"	150	340	42	1	8.3				
"	300	429	58	1	7.4				
"	300	382	62	1	14.0				
Tasmanian Sea ⁸	300	159	15	1	10.8				
"	1000	129	13	1	9.7				
"	300	193	22	1	8.8				
"	1000	232	22	1	10.5				
48° N ⁹	1000	968	110	1	8.8				
34° N ⁹	1000	430	74	1	5.8				
Sargasso Sea ¹⁰	3694	104	10	1	10.4				
tropical Atlantic ¹⁰	389	182	21	1	8.8				
"	976	274	31	1	8.9				
"	3755	180	18	1	10.3				
"	5068	202	20	1	10.3				
East Hawaii ¹⁰	378			1	9.0				
"	978			1	9.2				
"	2778	303	30	1	10.1				
"	4280	243	10	1	10.4				
"	5582			1	9.2				
Panama Basin ¹⁰	667	318	33	1	9.6				
"	1268	226	26	1	8.8				
"	2700	210	25	1	9.2				
"	3700	243	23	1	10.2				
Estimates from chemical data along isopycnals:									
N. Atlantic ¹¹	200–500					97±9	17.6±0.6	1	5.5
"	500–680					88±6	16.8±0.5	1	5.2
Atlantic, Indian, Pacific Ocean ¹²	500–1000					117±14	16±1	1	
N. Atlantic ¹³	200–500					101±12	14.4±0.7	1	7.2±0.4
"	500–680					131±18	16.8±1.3	1	7.8±0.5

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¹ This study, ^{2,3} Special Research Project (SFB313), University of Kiel, available at <http://www.ifm.uni-kiel.de/jgofs/dm/>. ⁴ Reigstad et al. (1999) ⁵ Struck et al. (2004). ⁶ Heiskanen et al. (1998) ⁷ Oceanic Flux Program of WHOI, ([urlstylesamehttp://www.whoi.edu/science/MCG/ofp/](http://www.whoi.edu/science/MCG/ofp/)) ⁸ Bray et al. (2000) ⁹ Honjo and Mangannini (1993) ¹⁰ Honjo et al. (1982) ¹¹ Takahashi et al. (1985) ¹² Anderson and Sarmiento (1984) ¹³ Körtzinger et al. (2001)

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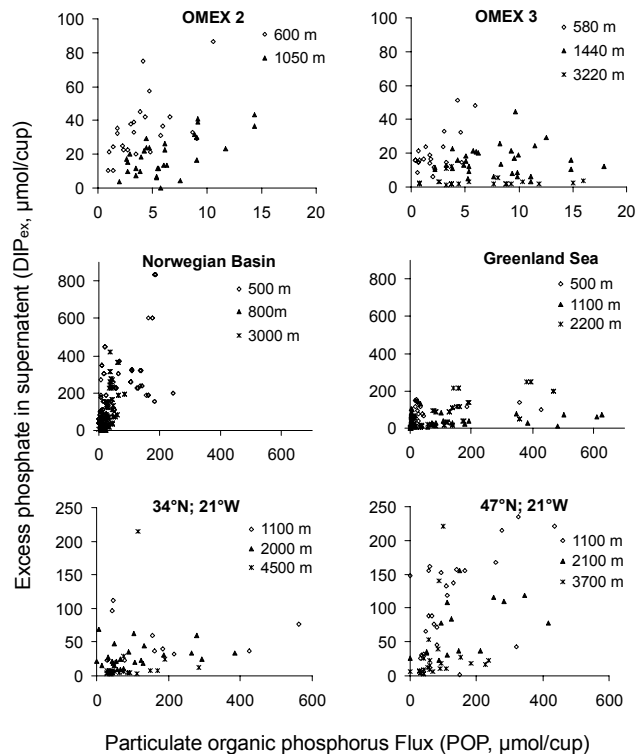


Fig. 1. Relationship between particulate organic phosphorus (POP) and excess dissolved phosphate (DIP_{ex}) in sediment trap samples at different sites and depths as listed in Table 1.

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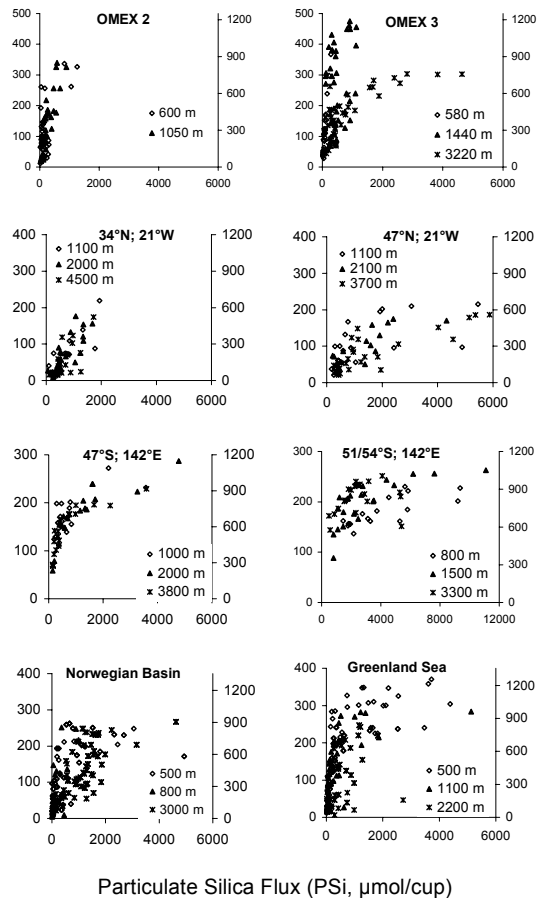
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Particulate Silica Flux (PSi, $\mu\text{mol}/\text{cup}$)

Fig. 2. Relationship between particulate biogenic silica (PSi) and excess dissolved silicic acid (DSi_{ex} , left axes) in sediment trap samples at different sites and depths as listed in Table 1. The absolute concentration of silicate in supernatant water is given on the right axes.

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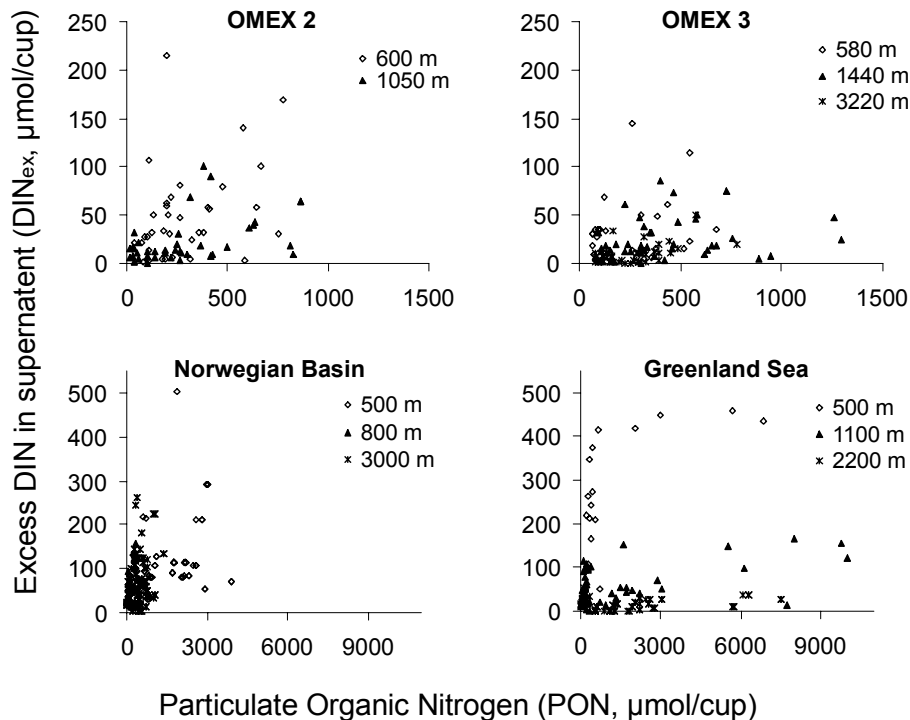


Fig. 3. Relationship between particulate organic nitrogen (PON) and excess dissolved inorganic nitrogen (ammonium and nitrate) (DIN_{ex}) in sediment trap samples at different sites and depths as listed in Table 1.

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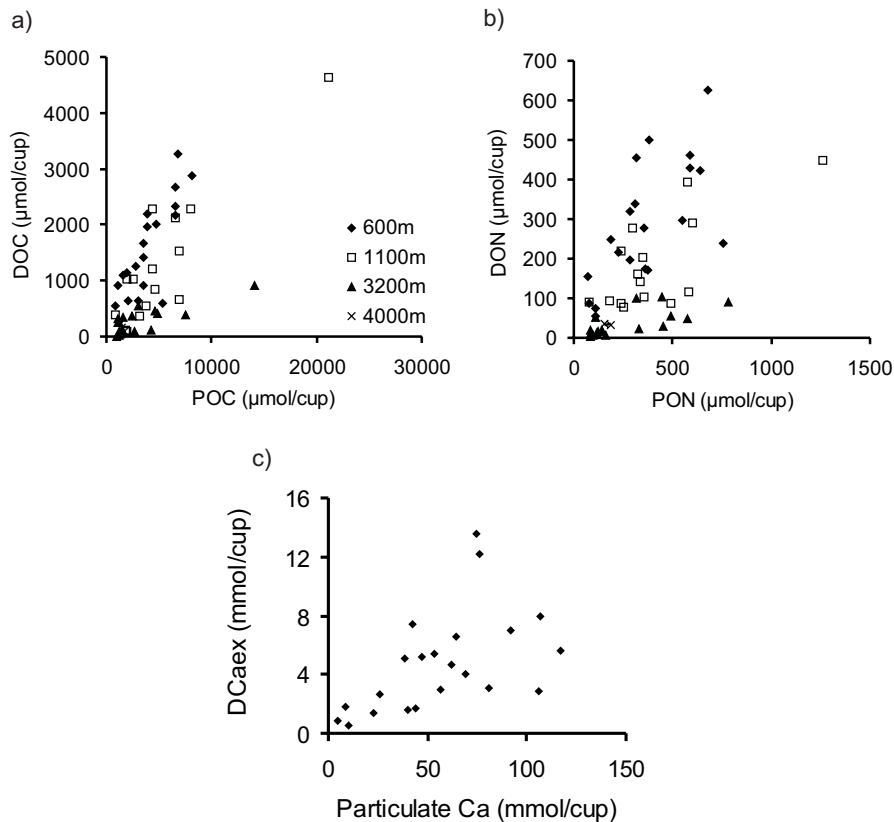


Fig. 4. Relationship between particulate organic carbon (**a**) and nitrogen (**b**) to the excess dissolved concentrations of organic carbon and nitrogen respectively. Relationship between particulate calcium and excess dissolved calcium in trap samples (**c**). All data are from the OMEX traps only.

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